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Tetrahedron Letters 47 (2006) 6957–6960
Tetrahedron Letters

A useful procedure for diiodination of carbazoles and subsequent efficient transformation to novel 3,6-bis(triethoxysilyl)carbazoles giving mesoporous materials

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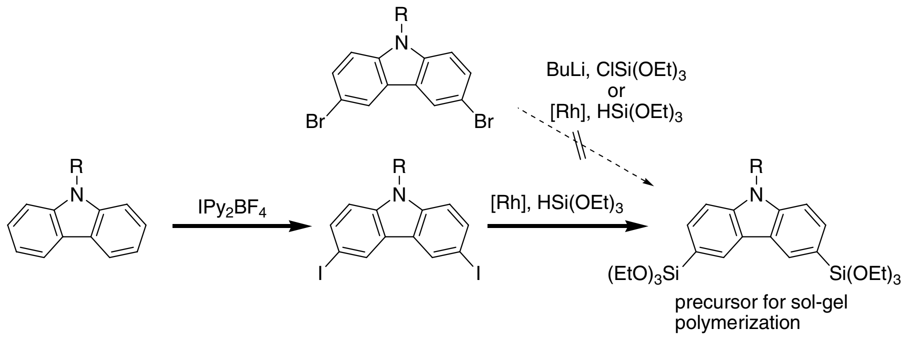
Received 30 June 2006; revised 20 July 2006; accepted 25 July 2006
Available online 14 August 2006

Abstract—Bis(pyridine)iodonium tetrafluoroborate (IPy_2BF_4) was successfully used as a diiodination reagent for carbazole and its derivatives to give 3,6-diiodocarbazoles in excellent yield. Subsequent rhodium-catalyzed disilylation of 3,6-diiodocarbazoles with triethoxysilane gave the corresponding 3,6-bis(triethoxysilyl)carbazoles, which are precursors for sol–gel polymerization, in good yield.

Organosilanes are useful building blocks for the preparation of organic–inorganic hybrid materials; to date, several types of organosilane precursor have been synthesized,[1] including arylene-bridged organosilanes, which are used in the synthesis of various bridged polysilsesquioxanes.[1b,c] We recently reported the synthesis of phenylene- and biphenylene-bridged mesoporous materials with crystal-like pore walls, which offer much potential as framework materials based on their stacking structures.[2] The incorporation of arylene groups as an integral component of the hybrid network gives rise to a number of promising organic–inorganic hybrid materials; however, it is very difficult to prepare the desired organosilanes in high yield by the conventional method, which involves lithiation of arylene dihalides followed by silylation, due to low solubility and inferior functional-group compatibility in the substrates and the difficulty of purifying the alkoxysilane products. Here, we disclose a facile preparation of novel carbazole-bridged trialkoxysilane derivatives which may be used as precursors for carbazole-skeleton hybrid materials (Scheme 1).

Carbazole derivatives have attracted a great deal of attention due to their potential as components of



Scheme 1.

Keywords: Rhodium catalyst; Silylation; Carbazole; Iodination.

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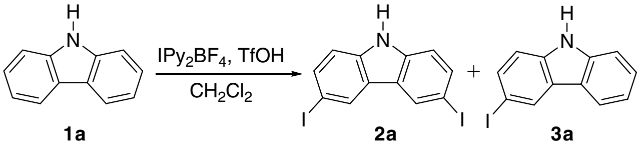
doi:10.1016/j.tetlet.2006.07.118

electroluminescent materials, thin-film transistors,[3] photochemical materials,[4] dendrimers,[5] nonlinear optical polymers[6] and active ligands for transition metal-catalyzed reactions.[7] However, to our knowledge there have been no reports describing the preparation of 3,6-bis(triethoxysilyl)carbazole as a precursor for functional materials.

First, we examined the lithiation of commercially available 3,6-dibromocarbazole with *n*-butyllithium followed by addition of chlorotriethoxysilane. Unfortunately, this reaction gave a mixture of many unidentified products, including trace amounts of the desired 3,6-bis(triethoxysilyl)carbazole. Recently, efficient palladium- and rhodium-catalyzed silylations of aryl halides with triethoxysilane were reported by the Masuda and coworkers[8a,b] and the DeShong and Manoso,[8c] respectively. Because aryl bromides have successfully been used as starting materials for rhodium-catalyzed silylation,[8b] we attempted to carry out this reaction using 3,6-dibromocarbazole and triethoxysilane; however, 3,6-dibromocarbazole was recovered unchanged. In general, cross-coupling reactions of aryl bromides often result in the absence of desired products, due to their reactive order toward transition metal-catalyzed reactions (ArI ≫ ArOTf > ArBr > ArCl);[9] carbazole and its derivatives are not exceptional in this respect. We decided to use 3,6-diiodocarbazole as a starting material for disilylation of carbazoles. Although several monoiodination reactions of carbazole have been reported,[10] there have been few reports of efficient preparation methods for 3,6-diiodocarbazole. Very recently, there have been reports of efficient iodination reactions of N-unsubstituted and N-substituted carbazoles in the presence of the required reagents.[11] During our investigation of iodination reactions, we found a further efficient diiodination reaction for N-unsubstituted carbazole, *N*-arylcarbazoles and *N*-alkylcarbazoles, developed by Barluenga et al., using bis(pyridine)iodonium tetrafluoroborate[12] (IPy_2BF_4).

Table 1. Iodination of N-unsubstituted carbazole[a]



Entry	IPy_2BF_4 (equiv)	TfOH (equiv)	**2a**/**3a**[b]	Yield of (**2a**+**3a**)[c] (%)
1	2	4	62:38	35
2[d]	3	6	—	0
3	2.5	1	100:0	96

[a] All reactions were carried out in CH_2Cl_2 at 25 °C for 20 h.

[b] Determined by NMR analysis.

[c] Isolated yield.

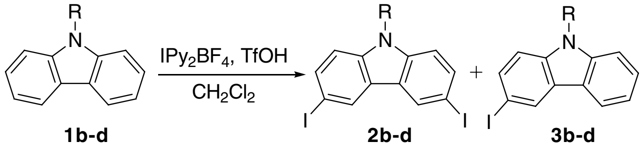
[d] Resulted in 1,3,6-triiodocarbazole.

In 2005, we reported a facile preparation of 5,5′-diiodo-BINAP using IPy_2BF_4, which opened the door to preparation of BINAP-based materials.[13] It is well known that carbazole undergoes electrophilic addition at the 3- and 6-positions. First, we carried out iodination of carbazole with 2 equiv of IPy_2BF_4 and 4 equiv of trifluoromethanesulfonic acid in dichloromethane at 25 °C for 20 h. However, this reaction gave an inseparable mixture of **2a** and **3a** in a 62:38 ratio in 35% yield, along with polyiodinated compounds and several unidentified byproducts (Table 1, entry 1).

Next, the use of excess IPy_2BF_4 and trifluoromethanesulfonic acid (3 equiv and 6 equiv, respectively) gave triiodinated carbazole in 71% isolated yield, without formation of **2a** or **3a** (Table 1, entry 2). These findings suggest that the use of excess trifluoromethanesulfonic acid relative to IPy_2BF_4 is not necessary for diiodination. We found that the reaction of 2.5 equiv of IPy_2BF_4 and 1 equiv of trifluoromethanesulfonic acid in dichloromethane at 25 °C for 20 h gave the desired product **2a** in 96% yield (Table 1, entry 3).[14]

We applied these optimized conditions to the reactions of N-substituted carbazoles (Table 2). The reaction of

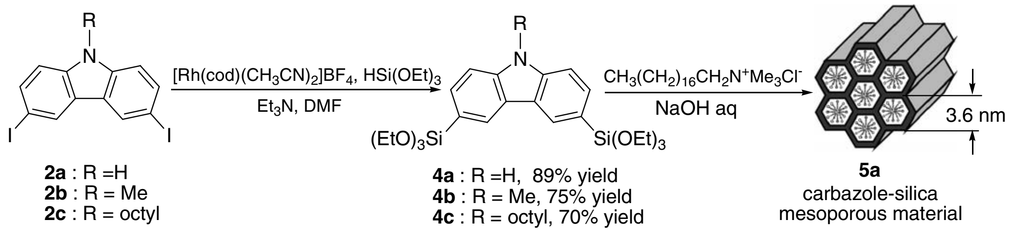
Table 2. Iodination of N-substituted carbazoles



Entry	R	IPy_2BF_4/TfOH (equiv)	Temperature (°C)	Time (h)	**2**/**3**[a]	Yield of (**2**+**3**)[b] (%)
1	Me (**1b**)	IPy_2BF_4 (2.5)/TfOH (1)	25	20	39:61	75
2		IPy_2BF_4 (2.5)/TfOH (1)	25	40	100:0	93
3	Oct (**1c**)	IPy_2BF_4 (2.5)/TfOH (1)	25	120	77:23	76
4		IPy_2BF_4 (2.5)/TfOH (1)	40	60	75:25	100
5		IPy_2BF_4 (2.5)/TfOH (1)	−30	20	8:92	97
6		IPy_2BF_4 (2.5)/TfOH (1)	−30	60	9:91	84
7		IPy_2BF_4 (2.5)/TfOH (2)	25	60	100:0	95
8	Ph (**1d**)	IPy_2BF_4 (2.5)/TfOH (1)	25	20	70:30	90
9		IPy_2BF_4 (2.5)/TfOH (2.5)	25	20	100:0	93

[a] Determined by NMR analysis.

[b] Isolated yield.



Scheme 2.

N-methylcarbazole at 25 °C for 40 h gave the corresponding iodinated compound **2b** in 93% yield, but the reaction was not completed within 20 h (Table 2, entries 1 and 2). The reaction of *N*-octylcarbazole gave an inseparable mixture of di- and monoiodinated compounds, and was not completed even with prolonged reaction times (Table 2, entry 3). While seeking the optimal reaction conditions, we found that the use of 2 equiv of trifluoromethanesulfonic acid at 25 °C for 60 h gave the desired product **2c** in excellent yield (95%; Table 2, entry 7). Furthermore, *N*-phenylcarbazole was successfully diiodinated to give *N*-phenyl-3,6-diiodocarbazole exclusively in an isolated yield of 93% (Table 2, entry 9).

The resulting diiodocarbazoles **2a**–**c** were subjected to rhodium-catalyzed disilylation with triethoxysilane, which proceeded smoothly to give the corresponding bis(triethoxysilyl)carbazoles **4a**–**c** in 89%, 75% and 70% yields,[15] respectively, although the use of 3,6-dibromocarbazole as a starting material under similar reaction conditions resulted in no reaction. In addition, we developed a purification method, using charcoal, for the resulting crude products **4a**–**c**, which allowed separation of the reduction product **1a**.[16] The purified **4a** was polymerized in 6 M sodium hydroxide in the presence of octadecyltrimethylammonium chloride to give carbazole–silica mesoporous material **5a** with a diameter of 3.6 nm (Scheme 2).[17] This novel preparation method for arylene-bridged organosilanes should allow the development of numerous promising precursors for sol–gel polymerization.

In summary, we have developed a useful method for diiodination of N-unsubstituted, *N*-methyl and *N*-octylcarbazoles with bis(pyridine)iodonium tetrafluoroborate followed by subsequent rhodium-catalyzed silylation with triethoxysilane at the 3,6-position to give the corresponding 3,6-bis(triethoxysilyl)carbazole derivatives in good yield.

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14. *General procedure for the diiodination of carbazole* (**1a**) *with bis(pyridine)iodonium tetrafluoroborate*. To a solution of bis(pyridine)iodonium tetrafluoroborate (278 mg, 0.75 mmol) and carbazole (**1a**) (50.0 mg, 0.30 mmol) in

dichloromethane (8 ml), was added dropwise trifluoromethanesulfonic acid (26.4 μL, 0.30 mmol) and the mixture was stirred at room temperature for 20 h. The reaction was quenched with saturated sodium thiosulfate solution and the mixture was extracted with dichloromethane. The organic phase was washed with brine and then with water, dried over sodium sulfate, and concentrated. The residue was chromatographed on silica gel (hexane–EtOAc = 5:1) to give 120.1 mg (96%) of 3,6-diiodocarbazole.

3,6-Diiodocarbazole (**2a**): 96% yield; ^{1}H NMR ($CDCl_3$) δ: 8.32 (d, $J = 1.9$ Hz, 2H), 8.09 (br, 1H), 7.68 (dd, $J = 8.4$ Hz, 1.9 Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 138.35, 134.68, 129.26, 124.44, 112.63, 82.41.

3,6-Diiodo-9-methycarbazole (**2b**): 93% yield; ^{1}H NMR ($CDCl_3$) δ: 8.32 (d, $J = 1.6$ Hz, 2H), 7.73 (d, $J = 8.6$ Hz, 1.6 Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 139.69, 134.30, 129.00, 123.60, 110.45, 81.67, 29.18.

3,6-Diiodo-9-octhylcarbazole (**2c**): 95% yield; ^{1}H NMR ($CDCl_3$) δ: 8.27 (d, $J = 1.6$ Hz, 2H), 7.67 (dd, $J = 8.4$ Hz, 1.6 Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.16 (t, $J = 7.0$ Hz, 2H), 1.80–1.75 (m, 2H), 1.28–1.21 (m, 10H), 0.85 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 139.15, 134.22, 129.06, 123.68, 110.70, 81.58, 43.15, 31.78, 29.33, 29.17, 28.82, 27.22, 22.65, 14.17.

3,6-Diiodo-9-phenylcarbazole (**2d**): 93% yield; ^{1}H NMR ($CDCl_3$) δ: 8.33 (d, $J = 2.2$ Hz, 2H), 7.63 (dd, $J = 8.6$ Hz, 2.2 Hz, 2H), 7.55 (d, $J = 7.0$ Hz, 2H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.41 (d, $J = 8.6$ Hz, 2H), 7.10 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ: 139.81, 136.44, 134.68, 129.94, 129.13, 127.93, 126.73, 1124.19, 111.80, 82.88.

15. *General procedure for the rhodium-catalyzed disilylation of 3,6-diiodocarbazole* (**2a**) *with triethoxysilane*. To a mixture of $[Rh(CH_3CN)_2(cod)]BF_4$ (45 mg, 0.12 mmol) and 3,6-diiodocarbazole (**2a**) (1.00 g, 2.39 mmol) was added distilled DMF (20 mL) and triethylamine (1.99 mL, 27 mmol). The mixture was stirred at room temperature for 30 min, after which triethoxysilane (1.76 mL, 18 mmol) was added dropwise, and stirring was continued at 80 °C for 7 h. The reaction mixture was then concentrated under vacuum to remove DMF. The resulting mixture was treated with Et_2O to obtain a solution of 3,6-bis(triethoxysilyl)carbazole in Et_2O, which was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The combined filtrates were concentrated under vacuum and the residue was passed through charcoal to give pure 3,6-bis(triethoxysilyl)carbazole (1.10 g, 89%).

3,6-Bis(triethoxysilyl)carbazole (**4a**): 89% yield; ^{1}H NMR ($CDCl_3$) δ: 8.46 (d, $J = 0.8$ Hz, 2H), 8.26 (s, 1H), 7.72 (dd, $J = 7.8$ Hz, 0.8 Hz, 2H), 7.43 (dd, $J = 7.7$, 0.8 Hz, 2H), 3.93 (q, $J = 7.3$ Hz, 12H), 1.29 (t, $J = 7.3$ Hz, 18H); ^{13}C NMR ($CDCl_3$) δ: 140.85, 131.83, 127.39, 122.70, 119.78, 110.49, 58.72, 18.29; HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{37}NO_6Si_2$, 490.2081 $(M-H)^-$; found, 490.2073.

3,6-Bis(triethoxysilyl)carbazole-9-methylcarbazole (**4b**): 75% yield; ^{1}H NMR ($CDCl_3$) δ: 8.49 (s, 2H), 7.79 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 2H), 3.95 (q, $J = 7.1$ Hz, 12H), 3.84 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 18H); ^{13}C NMR ($CDCl_3$) δ: 142.25, 131.90, 127.49, 122.45, 119.50, 108.18, 58.72, 29.10, 18.35; HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{39}NO_6Si_2$, 528.2214 $(M+Na)^+$; found, 528.2211.

3,6-Bis(triethoxysilyl)carbazole-9-octylcarbazole (**4c**): 70% yield; ^{1}H NMR ($CDCl_3$) δ: 8.49 (s, 2H), 7.77 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.1$ Hz, 2H), 4.29 (t, $J = 7.3$ Hz, 2H), 3.94 (q, $J = 7.3$ Hz, 12H), 1.89–1.84 (m, 2H), 1.32–1.18 (m, 28H), 0.86 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 141.70, 131.78, 127.50, 122.48, 119.32, 108.41, 58.70, 43.09, 31.80, 29.38, 29.18, 28.99, 27.31, 22.65, 18.35, 14.13; HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{53}NO_6Si_2$, 626.3309 $(M+Na)^+$; found, 626.3346.

16. Fortunately, mono silylated products including the mono reduction products were not observed.

17. *General procedure for sol–gel polymerization of* **4a**. Octadecyltrimethylammonium chloride ODTMA (0.087 g) was dissolved in a mixture of ion-exchange water (6 mL) and 6 M sodium hydroxide aqueous solution (0.1 mL). To the solution was added **4a** (100 mg), and the mixture was stirred at room temperature for 24 h. The solution was kept at 60 °C for 24 h under static conditions. The resulting white precipitate was recovered by filtration to give the desired mesoporous carbazole–silica material **5a** of 60 mg.